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(54) Title: COMPOSITION AND METHOD FOR INHIBITING THE CURE OF CYANOACRYLATE ADHESIVES AND CURE INHIBITED CYANOACRYLATE ADHESIVE COMPOSITIONS (57) Abstract Compositions and methods for inhibiting the cure of cyanoacrylate adhesives and cure inhibited cyanoacrylate adhesive compositions. The cure inhibited compositions comprise an organic carboxylic acid; and a hydrated or anhydrous metal chloride, fluoride, bromide or iodide.		

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COMPOSITION AND METHOD FOR INHIBITING THE
CURE OF CYANOACRYLATE ADHESIVES AND CURE-
INHIBITED CYANOACRYLATE ADHESIVE COMPOSITIONS

Background of the Invention

Field of the Invention

This invention relates to compositions containing cyanoacrylate adhesives that are temporarily inhibited from polymerizing and curing even in the presence of activating substances, such as metals, which normally catalyze polymerization of cyanoacrylate adhesive compositions. This invention also relates to compositions and methods for inhibiting polymerization and curing of cyanoacrylate adhesives.

20

Description of the Prior Art

A major drawback of cyanoacrylate compounds is their tendency to polymerize rapidly and often uncontrollably when contacted or mixed with various activating substances, especially substances that form ions in solution. Even trace quantities of such activators as organic salts, inorganic salts, metals, water, urea, oxides, etc., substantially increase the rate of cyanoacrylate polymerization. This tendency has limited the usefulness of cyanoacrylate compounds to ordinary adhesive applications. If cyanoacrylate compounds could be mixed with sufficient quantities of various activating substances without polymerizing immediately, they would be useful in a wide variety of additional applications.

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The development of cyanoacrylates, such as methyl-2-cyanoacrylate, ethyl-2-cyanoacrylate, propyl-2-cyanoacrylate, 2-ethylhexyl-2-cyanoacrylate, isobutyl-2-

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1 cyanoacrylate, n-butyl-cyanoacrylate, hexyl-, heptyl-, and
octyl-cyanoacrylate, etc., represented a major technological
advance in the bonding and adhesive art.

The preparation of cyanoacrylates is well-known.
5 It is described in such U.S. Patents as No. 2,467,926; No.
2,794,788; No. 2,912,454; and No. 2,926,188, the disclosures
of which are incorporated by reference. The use of cyano-
acrylate polymers as adhesives is described in such U.S.
Patents as No. 2,776,232; No. 2,794,788; and No. 2,467,926,
10 also incorporated by reference. The cyanoacrylate adhesives
are fast-drying, high tensile-strength glues and bonding
agents. Their use in bonding or joining materials together
is very widespread in industry, in the household, and in
special applications such as surgery (as tissue adhesives),
15 dentistry, etc.

Various inorganic substances have been proposed
as fillers or thickeners for cyanoacrylate monomer composi-
tions. For example, U.S. Patent No. 3,663,501 of Adams, et
al. issued on May 16, 1972 discloses preparation of a
20 dental cement containing finely divided sodium fluoride,
fused silica, quartz, and alumina fillers. U.S. Patent No.
3,607,542 of Leonard, et al. issued on September 21, 1971
discloses the preparation of water-resistant cyanoacrylate
paste containing insoluble inert fillers (such as various
25 salts of calcium, titanium, zinc, tin, aluminum and iron)
for use as adhesives in submerged applications and as
fillings for teeth. Neither reference is concerned with
the polymerization rate of cyanoacrylate adhesives or with
its control.

30 Incorporation of acid inhibitors in cyanoacrylate
compositions is known. For example, U.S. Patent NO.
4,182,823 of Schoenberg issued on January 8, 1980 teaches
that acid additives called "stabilizers" in the patent)
including acid gases, other acids (such as acetic) or
various Lewis acids (such as FeCl_3 , SnCl_2 and BF_3) inhibit
35 polymerization of cyanoacrylate compositions. The patent
warns, however, that such additives must be used with

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1 caution because strong acids "over-stabilize" the monomer
and weak acids do not "stabilize" it sufficiently. Schoen-
berg further observes that the acids (which are said to act
as anionic polymerization inhibitors) interfere with the
5 cure of the adhesive.

U.S. Patent No. 2,794,788 of Coover issued on
June 4, 1957 states that sulfur dioxide is effective as a
stabilizer for cyanoacrylate monomers, that boron trifluo-
ride and hydrogen fluoride are also effective, but that
10 carbon dioxide is less effective.

U.S. Patent No. 4,460,759 of Robins issued July
17, 1984 discloses a two-part cyanoacrylate adhesive compo-
sition. One part of this composition contains weakly
acidic or weakly ionic compounds as accelerators for
15 polymerization, particularly when these compositions are
used on wood substrates. Such accelerators are said to
include metal halides. The first part contains acid gases
and free-radical compounds as inhibitors.

Although many of the above references recognize
20 the need to control the rate of polymerization of cyano-
acrylate adhesives, the additives they propose are inade-
quate as inhibitors because their inhibitory effect cannot
be well-controlled.

As stated in Schoenberg, supra, too little
25 acid inhibitor is not effective and too much can interfere
with polymer cure. In addition, many acid additives cause
polymer decomposition, and shorten the useful life of the
cyanoacrylate polymer.

Accordingly, it is an object of the present
30 invention to provide novel compositions useful as inhibitor-
stabilizers for cyanoacrylate compounds and compositions.

Another object is to provide novel inhibiting-
stabilizing compositions for cyanoacrylates that effective-
ly delay onset and propagation of polymerization reactions
even in the presence of activators for such reactions.
35

Another object is to provide cyanoacrylate compo-
sitions that are temporarily or permanently rendered non-
reactive to activating substances.

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1 Another object of the invention is to provide cyanoacrylate compositions that are temporarily or permanently inhibited from polymerizing in which the inhibitor does not cause premature decomposition of the polymer.

5 Another object is to provide cyanoacrylate compositions that are temporarily or permanently inhibited from polymerizing to a controlled extent although they contain substantial amounts of substances that act as catalysts for cyanoacrylate polymerization.

10 Another object is to provide cyanoacrylate compositions that are electrically or thermally conductive and have such polymerization and stability characteristics or mechanical properties as make them suitable for use in the manufacture of electronic and microelectronic components.

15 Another object is to expand the uses to which cyanoacrylate adhesive compositions can be put by providing compositions comprising cyanoacrylate monomers that are controllably inhibited towards polymerization and at the same time yield polymers with the desired degree of
20 cure and stability.

 A further object is to prepare cyanoacrylate adhesive compositions that can be spray-coated in place using inter alia on artists' air brush.

 Yet another object is to provide methods for
25 inhibiting the polymerization of cyanoacrylate compounds and for preparing polymerization-inhibited and stabilized compositions containing cyanoacrylate compounds and activators.

Summary of the Invention

30 One aspect of this invention is directed to a composition comprising at least one organic acid and at least one hydrated or anhydrous base metal fluoride, chloride, bromide or iodide. The composition is useful in inhibiting-stabilizing cyanoacrylates.

35 Another aspect of the invention is directed to a cyanoacrylate composition temporarily or permanently inhibited from polymerizing, the composition including an

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1 organic acid and at least one hydrated or anhydrous metal fluoride, chloride, bromide or iodide. The composition may include a filler that is ordinarily an activator of cyanoacrylate polymerization.

5 Yet another aspect of the invention relates to a method for inhibiting cyanoacrylates against polymerization by incorporating either to said cyanoacrylates or to an activator additive thereof an inhibitor comprising a liquid organic acid and an anhydrous or hydrated metal fluoride,
10 chloride, bromide or iodide, prior to mixing said cyanocrylate with said activator-additive, or simultaneously therewith.

DETAILED DESCRIPTION OF THE INVENTION

15 In accordance with the present invention, unpolymerized (or partially polymerized) cyanoacrylate compositions can be temporarily (or permanently) inhibited from reacting with polymerization-activating materials (activators) and at the same time stabilized against incomplete cure and/or premature decomposition.

20 This inhibition-stabilization of the cyanoacrylate is accomplished by incorporating an inhibitor-stabilizer either in the unpolymerized (or partially polymerized) cyanoacrylate or in an activator that will serve as an additive or filler of the final composition, said inhibitor-stabilizer comprising:
25

- (a) an organic carboxylic acid; and
- (b) a hydrated or anhydrous metal chloride, fluoride, bromide or iodide.

30 The inhibitor-stabilizer is preferably incorporated in the cyanoacrylate adhesive (monomer or prepolymer) prior to exposure of the latter to an activator, such as a metal, oxide, ionic solvent, salt, water or urea. However, it can also be incorporated to the activator prior to mixing it with the cyanoacrylate. The ingredients of the
35 inhibitor-stabilizer must be premixed and may not be separately incorporated in the cyanoacrylate or activator.

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1 Preferably, the inhibitor-stabilizer also in-
cludes a polar solvent to facilitate mixing with and
solubility in the cyanoacrylate (or activator additive).
In fact, unless the two active ingredients of the inhibitor-
5 stabilizer are fully compatible with the cyanoacrylate (or
activator-additive), use of a solvent is particularly
desirable. Additional solvent may be used when the in-
hibitor-stabilizer is mixed with the cyanoacrylate to
facilitate mixing. This additional solvent may but need
10 not be a polar solvent; it can be any suitable organic
solvent.

Suitable solvents for the inhibitor include polar
organic and inorganic solvents, such as water, lower
aliphatic alcohols, lower aliphatic ketones, lower aliphatic
15 ethers of carboxylic acids, lower alkylene glycols, lower
alkylene glycol ethers, lower aliphatic esters of carboxylic
acids, carboxylic acid nitriles, and mixtures thereof.
Methyl chloride, formaldehyde and dimethyl sulfoxide are
also useful as solvents in the present invention.

20 Preferred solvents are: water; acetone, methyl
ethyl ketone, methyl propyl ketone, methyl isobutyl ketone,
ethyl butyl ketone, acetyl acetone; methanol, ethanol,
propanol, isopropanol, butanol, isobutanol, and hexanol,
ethyl acetate, propyl acetate, isopropyl acetate, butyl
25 acetate, and methyl-CELLOSOLVE^R-acetate (methyl-2-ethoxy-
ethanol acetate; CELLOSOLVE^R is a trademark of Union
Carbide Corporation); ethyl ether, dimethyl ether, and
diethylene glycol ethyl ether (diethyl-CARBITOL^R; a trade-
mark of Union Carbide Corporation); methyl-CELLOSOLVE, butyl
30 CELLOSOLVE, methyl glycol ether, butoxy triglycol, methoxy
triglycol, glycol methyl CARBITOL; and acetonitrile.

The most preferred solvents for use in the
present invention are: water, acetone, ethanol, ethyl
acetate, dimethyl ether, glycol methyl CARBITOL, and
35 acetonitrile.

Preferred acids for the inhibitor-stabilizer
are formic acid, acetic acid, propionic acid, butanoic

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1 acid, lactic acid, pentenoic acid, carbonic acid, etc.
Most preferred is formic acid.

Preferred metal halide salts are: FeCl_3 ;
 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; LiF ; CdCl_2 ; $\text{CdCl}_2 \cdot 2-1/2\text{H}_2\text{O}$; $\text{MgBr} \cdot 6\text{H}_2\text{O}$;
5 SnBr_4 ; GeCl_4 ; MgCl_2 ; ZnCl_2 ; ZnBr ; $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$;
 $\text{LiI} \cdot 3\text{H}_2\text{O}$; $\text{LiI} \cdot \text{H}_2\text{O}$; $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$; and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. Magnesium
bromide hexahydrate, tin chloride hexahydrate and ferric
chloride hexahydrate are most preferred.

Non-polar solvents that can be added to the in-
hibited cyanoacrylate composition include without limita-
10 tion plasticizers, such as dibutyl phthalate, tricresyl
phosphate, dimethyl phthalate, etc.

Generally suitable relative proportions of the
ingredients of the inhibitor-stabilizer, i.e. the acid,
15 salt and solvent (if any) are: acid -- about 0.002 - 55%;
salt -- about 0.002 - 50%; and solvent -- about 0 - 75% by
weight.

As a weight percentage of the cyanoacrylate
monomer the inhibitor-stabilizer can be about 0.10-55%.

20 The above proportions are given by way of guide-
lines. The actual amount of the inhibiting-stabilizing
composition will depend on how long it is desired to delay
the onset of polymerization for the final cyanoacrylate
mixture (i.e. after addition of the activating substance)
25 and, to a lesser extent, on the ability of the activator to
catalyze cyanoacrylate polymerization. It should be noted
that as the percentage compositive of acid and salt is
increased, the cure time of the adhesive composition
increases.

30 The duration of the stabilization or inhibition
provided by a given stabilizer/acrylate formulatin is also
dependent upon the ambient temperature to which the material
is exposed. Storage of an inhibited cyanoc rylate compound
of the present invention at 120°F for 3 weeks would result
35 in some curing of the adhesive, however, if the same
composition were stored at 40°F for 3 months little or no
curing would take place.

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1 By varying the ratio of inhibitor ingredients to
cyanoacrylate constituents in the present invention, it is
possible to inhibit curing for periods varying between a
few minutes and
5 several months.

The incorporation of the inhibitor-stabilizer
renders the cyanoacrylate non-reactive to activating
substances for a period of time at least long enough to
permit mixing of the cyanocrylate with the activator and
10 any processing, storage, or fabrication necessary for the
particular end application envisioned.

By the present invention, a multitude of applica-
tions become possible. The following are listed for
illustration purposes only.

15 1) Electrically Conductive Cyanoacrylate
Compositions and Materials

Incorporation of a metal with high conductivity
(in powder or other particulate form) as a filler can
render a cyanoacrylate composition electrically conductive.
20 Before the present invention, it was impossible to incorpo-
rate sufficient metal as a filler to render the polymer
electrically conductive because rapid polymerization of the
cyanoacrylate would begin immediately following addition
of even minute quantities of metal. This made further
25 addition of metal impossible. Moreover, rapid polymeriza-
tion of the metal-filled cyanoacrylate would interfere with
the processing or fabrication of the finished product.

Metal-filled cyanoacrylate polymers can be
used in die and wire bonding of microelectronic circuits
30 instead of solder. In addition, they can be used as
conductive terminals for resistors, as electrodes for
capacitors and for a variety of functions in thick-film
hybrid microelectronic circuits. The metal-filled cyano-
acrylate compositions can be applied to circuit boards by
35 conventional screening methods. Electrically conductive
cyanoacrylate compositions preferably contain about 0.5 -

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1 7.0% of inhibitor, 0.05 - 0.4% acid, 0.08 to 0.8% salt and
about 0.4% to 10.0% solvent by weight of the cyanoacrylate
monomer.

5 Other applications for conductive cyanoacrylates
are in high-conductivity metallization films and coatings
for plastics, paper, mica, ceramics and other non-conductive
materials. The metallized films and coatings allow direct
soft-soldering without the use of flux and may be further
10 metal-coated by electroplating. Such films and coatings
are useful in electronic and microwave applications as
connectors, contacts, magnetic shields, especially in metal
shields that are used to protect from Radio Frequency
Interference (RFI) and Electro Magnetic Interference (EMI)
and capacitor terminals. They can be applied by brushing,
15 dipping, or spraying, or by conventional screening tech-
niques using standard 180 to 200 mesh screens.

These conductive, film-forming cyanoacrylate
compositions preferably contain about 1.0 - 7.0% inhibitor-
stabilizer (0.07 to 0.6 acid, 0.2 to 1.3% salt) and about
20 1.0 - 10.0% solvent.

Suitable metal fillers for electrically conduc-
tive cyanoacrylates, in general, include one or more of
palladium, silver, copper, tin, gold, and platinum and
other high-conductivity metals. The metal filler may first
25 be combined with the inhibitor composition and the metal-
containing inhibitor may subsequently be introduced into
the cyanocrylate. This makes it possible to package these
constituents separately for mixing by the consumer just
prior to use (as an A&B component system).

30 2) Thermally Conductive Cyanoacrylate
Compositions and Materials

Incorporation of fillers can also produce thermo-
conductive materials that can be used as heat sinks for
the base and mounting stud of transistors, diodes, and
35 rectifiers; and as coupling agents to reduce thermal
contact resistance. Suitable fillers for this purpose
include base metals, such as iron, aluminum, tin, and metal
oxides that are not electrically conductive, etc.

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1 Another use for thermally conductive cyanoacryl-
ates is for application between, e.g., semiconductor power
devices and heat sinks; power resistors and chassis mounts;
thermostats and mounting surfaces; and anywhere else where
5 the efficient transfer and removal of heat are necessary or
desirable. Finally, they can be used in thermoelectric
devices (e.g. in transformers as anti-static layers and
heat sinks) and in heat dissipaters for electronic devices.
Suitable fillers for this purpose are base metal oxides
10 (especially alumina) and iron, graphite, titanium, tin;
gold, silver, copper and all heavy metals.

Thermally conductive cyanoacrylate compositions
according to this invention preferably contain about 1.0 to
7.0% inhibitor 0.07 to 0.6% acid, 0.2 to 1.3% salt and
15 about 1-11% solvent.

The thermally conductive cyanocrylates of the
present invention can be used in place of other thermocon-
ductive plastic materials including thermoconductive
expoxies containing alumina or other metals. These thermal
20 cyanoacrylates may be employed to join heat sinks and other
components to printed circuit boards and in like applica-
tions.

3) Photoconductive Cyanoacrylate
Compositions and Materials

25 In general, these are liquid or screenable paste
(slurry) compositions that can be used in the manufacture
of photocells used for light sensors, light-controlled
relay operations, exposure meters, fire detectors, photo-
meters, lamp controls, liquid level indicators and a
30 variety of other detectors. Suitable fillers include
cadmium sulfide, cadmium selenide and cadmium-sulfoselenide.
Compositions used in these applications preferably contain
about 0.5 - 0.2% acid about 0.08 - 0.24% salt and about 1
- 11% solvent.

35 It will be understood by those skilled in the art
of the present invention that a variety of other fillers

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1 can be incorporated to the inhibited-stabilized cyanoacryl-
ates contemplated herein. These include one or more of
plasticizers, silicones, silica, polymeric fillers, fibers,
magnetic resins, pharmaceuticals, dyes, water, non-polar
5 solvents, radioactive materials, viscosity modifiers, human
and animal skin, etc.

This invention is for use with any cyanoacrylate
monomer (or prepolymer) including but not limited to those
set forth in the Background of the Invention, or mixtures
10 thereof.

The invention will be further described below
by reference to specific examples, which are intended to
illustrate it without limiting its scope. Thus, the scope
of the present invention is not to be limited to the
15 cyanoacrylates, fillers, acids, salts and solvents or
proportions disclosed in the Examples, below.

EXAMPLE 1

A stabilizing-inhibiting composition with or without
a solvent is formed by mixing the following ingredients:

Formula (A)40.7% $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$

40.7% Water

18.6% Formic Acid

Formula (B)15.9% $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$

15.9% Water

7.3% Formic acid

30.5% Acetone

30.5% Ethyl Cellosolve

Formula (C)23.5% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$

23.5 Acetone

53.0% Formic Acid

Formula (D)50.0% $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$

50.0% Acetic Acid

Formula (E)15.9% $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$

30.5% Butoxyethylene glycol

15.9% H_2O

7.3% Formic acid

30.5% Acetone

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EXAMPLE 2

An inhibited-stabilized methyl-2-cyanoacrylate composition is made by mixing one of the stabilizing-inhibiting compositions according to Example 1 with methyl-2-cyanoacrylate monomer and a solvent to improve mixing. The resulting compositions in weight percent are shown in the table below:

Inhibited Cyanoacrylate	I	II	III	IV
<u>Composition No.</u>				
Inhibitor (Any one of Ex. 1)	0.05	0.5	18.0	0.8
Acetone	2.0	2.0	3.0	0.8
Methyl Cyanoacrylate	97.95	97.5	76.0	98.2
Methyl-CELLOSOLVE ^R	_____	_____	_____	0.2
Ethyl Acetone	_____	_____	3.0	_____

EXAMPLE 3

An electrically conductive cyanoacrylate composition is formed from the inhibited-stabilized compositions No. II of Example 2 and the following ingredients:

Inhibited-Stabilized C.A.	84.0 (II)	50.0 (II)	35.0 (II)
Gold Powder	16.0	_____	_____
Silver Powder	_____	37.0	_____
Tin Powder	_____	_____	65.0
Copper Powder	_____	13.0	_____
	100.00	100.00	100.00

These compositions will not polymerize for about 24 hours from incorporation of the metal powders.

EXAMPLE 4

A thermoconductive cyanoacrylate composition is formed from the inhibited-stabilized cyanoacrylate compositions No. III of Example 2 and the following ingredients:

Inhibited-Stabilized C.A.	50.0 (III)	49.0 (III)	54.0 (III)
Copper Powder	50.0	_____	_____
Iron Powder	_____	40.0	_____
Thulium Powder	_____	_____	36.0
Tungsten Powder	_____	21.00	10.0

The thermoconductive compositions will not polymerize for about 24 hours from incorporation of the metal powders.

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1 EXAMPLE 5

A fiber-filled cyanoacrylate composition is prepared as outlined above, except that the cyanoacrylate compositions No. IV and II were used.

5	Inhibited-Stabilized C.A.	85.0 (IV)	92.0 (II)
	Paper Fiber	5.0	<hr/>
	Wool Fiber	10.0	8.0

These compositions will not polymerize for about 24 hours after incorporation of the fibers. They can be used as adhesives, especially in high impact resistant applications and in joining sheet and cloth materials (e.g. textile fabrics, leather and vinyl sheets).

10 EXAMPLE 6

A flexible plasticized cyanoacrylate composition for use as a caulking material is prepared by mixing the inhibitor-stabilized cyanoacrylate of Example 2 with the following ingredients:

	Inhibited-Stabilized C.A.	99.2 (IV)	90.0 (II)
	Plasticizer		
20	[Propylene carbonate]	0.8	5.0
	Plasticized polyvinyl acetate	<hr/>	5.0

15 EXAMPLE 7

A sprayable cyanoacrylate composition containing finely divided silver particles was prepared by admixing a stabilized-inhibited cyanoacrylate composition (Formula I of Example 2 prepared with inhibitor Formula E of Example 1) with 30 percent by weight of the stabilized inhibited cyanocrylate composition of finely divided metallic silver particles (average size 200-300 mesh). The silver powder is stirred in with a single blade electric laboratory mixer until an essentially homogeneous silver dispersion is obtained. The silver containing cyanoacrylate mixture is loaded into the reservoir of a Badger brand artists' air brush. The brush is connected to a source of pressurized air (30-40 psi). Plastic sheets (each approximately 2" x 2" x 1/4") of Styrene, ABS and acrylic (plexiglass) were laid on a flat surface.

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1 A solution of 5% toluidine was coated on the
upper surface of the ABS plastic sheet and allowed to dry
at room temperature (15°C).

5 The silver-containing cyanoacrylate composition
was sprayed across the entire upper surface of the three
plastic sheets (with the nozzle of the air brush held
approximately eight inches from the surface of each sheet)
using broad sweeping strokes.

10 At the conclusion of the spraying operation, a
second sheet of styrene was applied to the cyanocrylate
sprayed surface of the first styrene sheet and pressed down
momentarily (using hand pressure).

The cyanocrylate on the ABS sheet cured in
approximately 3 minutes.

15 The cyanoacrylate joining the styrene sheets
cured to working condition (i.e. to a condition in which
the sheets could not be pulled apart by hand) in approxi-
mately fifteen minutes.

20 The cyanoacrylate on the acrylic sheet cured
within one hour.

25 The method for making the compositions of the
present invention employed in the specific embodiments
described above is basically the same regardless of the
particular cyanoacrylate, activator-filler and inhibitor-
stabilizer used.

30 As those skilled in the art will appreciate, many
modifications, additions, omissions and substitutions can
be made, all within the scope and spirit of the present
invention as claimed below.

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What is claimed is:

1. A composition useful in inhibiting polymerization of cyanoacrylate in the presence comprising from about 0.002 to about 55% of an organic acid or mixture of organic acids and from about 0.002 to about 50% of a salt selected from the group consisting of hydrated and anhydrous base metal chlorides, fluorides, bromides and iodides and mixtures thereof, said percentages being by weight.

2. The composition of claim 1 also comprising from 0 to about 75% of a polar solvent.

3. The composition of claim 2, said solvent being selected from the group consisting of water, aliphatic alcohols, lower alkylene glycols, lower alkylene glycol ethers, carboxylic acid nitriles and mixtures thereof.

4. The composition of claim 1, said acid being selected from the group consisting of formic acid, acetic acid, propionic acid, lactic acid, pentenoic acid, butyric acid, carbonic acid, and mixtures thereof.

5. The composition of claim 1, said salt being selected from the group consisting of: FeCl_3 ; $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; LiF ; CdCl_2 ; $\text{CdCl}_2 \cdot 2-1/2 \text{H}_2\text{O}$; $\text{MgBr} \cdot 6\text{H}_2\text{O}$; SnBr_4 ; GeCl_4 ; MgCl_2 ; ZnCl_2 ; ZnBr ; $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$; $\text{LiI} \cdot 3\text{H}_2\text{O}$; $\text{LiI} \cdot \text{H}_2\text{O}$; $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$; and mixtures thereof.

6. The composition of claim 3 said acid being selected from the group consisting of formic acid, acetic acid, propionic acid, lactic acid, pentenoic acid, butyric acid, carbonic acid and mixtures thereof.

7. The composition of claim 6, said salt being selected from the group consisting of: FeCl_3 ; $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; LiF ; CdCl_2 ; $\text{CdCl}_2 \cdot 2-1/2 \text{H}_2\text{O}$; $\text{MgBr} \cdot 6\text{H}_2$; SnBr_4 ; GeCl_4 ; MgCl_2 ; ZnCl_2 ; ZnBr ; $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$; $\text{LiI} \cdot 3\text{H}_2\text{O}$; $\text{LiI} \cdot \text{H}_2\text{O}$; $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$; and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and mixtures thereof.

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8. The composition of claim 4, said salt being selected from the group consisting of: FeCl_3 ; $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; LiF ; CdCl_2 ; $\text{CdCl}_2 \cdot 2-1/2 \text{H}_2\text{O}$; $\text{MgBr} \cdot 6\text{H}_2\text{O}$; SnBr_4 ; GeCl_4 ; MgCl_2 ; ZnCl_2 ; ZnBr ; $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$; $\text{LiI} \cdot 3\text{H}_2\text{O}$; $\text{LiI} \cdot \text{H}_2\text{O}$; $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$; and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and mixtures thereof.

9. The composition of claim 1, said acid being formic acid.

10. The composition of claim 1, said salt being selected from the group consisting of $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{MgBr} \cdot 6\text{H}_2\text{O}$; $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; and mixtures thereof.

11. The composition of claim 3, said acid being formic acid.

12. The composition of claim 3, said salt being selected from the group consisting of $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{MgBr} \cdot 6\text{H}_2\text{O}$; $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; and mixtures thereof.

13. The composition of claim 11, said salt being selected from the group consisting of $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{MgBr} \cdot 6\text{H}_2\text{O}$; $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; and mixtures thereof.

14. The composition of claim 9, said salt being selected from the group consisting of $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{MgBr} \cdot 6\text{H}_2\text{O}$; $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; and mixtures thereof.

15. The composition of claim 14, said solvent being selected from the group consisting of water, acetone, acetonitrile, ethanol, ethylene glycol, ethyl acetate, dimethyl ether, and glycol methyl carbitol.

16. The composition of claim 15 comprising about 1 - 55% of said acid and about 1 - 45% of said salt.

17. The composition of claim 16 comprising about 5 - 40% of said acid, about 5 - 40% of said salt and about 1 - 60% of said solvent.

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18. An adhesive composition comprising:

- (a) a monomeric ester of cyanoacrylic acid; and
- (b) an inhibitor comprising:

- (i) an organic acid and (ii) a metal halide salt; said composition being inhibited from polymerizing when mixed with polymerization-activating substances.

- (ii) a metal salt selected from the group consisting of FeCl_3 ; $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; LiF ; CdCl_2 ; $\text{CdCl}_2 \cdot 2-1/2 \text{H}_2\text{O}$; $\text{MgBr} \cdot 6\text{H}_2\text{O}$; SnBr_4 ; GeCl_4 ; MgCl_2 ; ZnCl_2 ; ZnBr ; $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$; $\text{LiI} \cdot 3\text{H}_2\text{O}$; $\text{LiI} \cdot \text{H}_2\text{O}$; $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$; and mixtures thereof;

said composition being inhibited from polymerizing when mixed with polymerization-activating substances.

19. The composition of claim 18 wherein said acid is selected from the group consisting of formic acid, acetic acid, propionic acid, lactic acid, pentenoic acid, butyric acid, carbonic acid, and mixtures thereof.

20. The composition of claim 19, wherein said solvent is selected from the group consisting of water, acetone, acetonitrile, ethanol, ethylene glycol, ethyl acetate, dimethyl ether, and glycol methyl carbitol.

21. The composition of claim 20, wherein said inhibitor is present in an amount between about 0.1% and about 50% by weight based on said cyanoacrylic acid monomer.

22. The composition of claim 21, wherein said inhibitor is present in an amount between about 1 and about 20% by weight based on said cyanoacrylic acid monomer.

23. A composition according to claim 22 further comprising a solvent selected from the group consisting of water, acetone, acetonitrile, ethanol, ethylene glycol, ethyl acetate, dimethyl ether, and glycol methyl carbitol.

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24. A composition according to claim 23 wherein said inhibitor is present in an amount between about 1 and about 25% and said solvent is present in an amount between 0 and about 60% based on said monomer.

25. A composition according to claim 24, said composition further comprising a substance selected from the group consisting of activators that would catalyze polymerization of said monomer but for the presence of said inhibitor.

26. A composition according to claim 25, said composition being an electrically conductive composition.

27. A composition according to claim 26, said composition being a thermally conductive composition.

28. A composition according to claim 27, said composition being a photoconductive composition.

29. A method for stabilizing a cyanoacrylate adhesive composition so that said composition is inhibited from polymerizing when mixed with substances activating said polymerization, said method comprising:

adding to said composition in an amount effective to inhibit said polymerization an inhibitor comprising:

(a) an organic said selected from the group consisting of formic acid, acetic acid, propionic acid, lactic acid, pentenoic acid, butyric acid, carbonic acid, and mixtures thereof;

(b) a salt selected from the group consisting of FeCl_3 ; $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; LiF ; CdCl_2 ; $\text{CdCl}_2 \cdot 2-1/2 \text{H}_2\text{O}$; $\text{MgBr} \cdot 6\text{H}_2\text{O}$; SnBr_4 ; GeCl_4 ; MgCl_2 ; ZnCl_2 ; ZnBr ; $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$; $\text{LiI} \cdot 3\text{H}_2\text{O}$; $\text{LiI} \cdot \text{H}_2\text{O}$; $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$; and mixtures thereof;

prior to or simultaneously with addition of an activating substance.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/01047

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ²
 According to International Patent Classification (IPC) or to both National Classification and IPC C09K 3/00; H01B 1/02
 INT. CL.4 C08F 20/42, 4/06; C08J 3/14, 3/16; C08L 37/00, 39/00; H01C 13/00
 US CL. 252/380, 501.1, 512; 256/188.31; 156/331.2; 524/548; 526/100, 298

II. FIELDS SEARCHED

Minimum Documentation Searched ⁴	
Classification System	Classification Symbols
U.S.	526/100, 298; 156/331.2; 252/188.31, 380, 501.1, 512; 524/548

Documentation Searched other than Minimum Documentation
 to the Extent that such Documents are Included in the Fields Searched ⁵

III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴

Category ⁶	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	US, A, 4,182,823, Published 08 JANUARY 1980, SCHOENBERG. See the entire document.	1-29
X	UK, A, 2,078,763, Published 13 JANUARY 1982, KOSUKE LIDA. See the entire document.	1-29
Y	US, A, 4,125,494, Published 14 NOVEMBER 1978, SCHOENBERG. See the entire document.	1-29
Y	US, A, 3,968,186, Published 06 JULY 1976, TOMASCHEK ET AL. See the entire document.	1-29
Y	US, A, 4,460,759, Published 17 JULY 1984, ROBINS. See the entire document.	1-29
Y	US, A, 3,254,111, Published 31 MAY 1966, HAWKINS ET AL. See the entire document.	1-29
Y	US, A, 3,527,841, Published 08 SEPTEMBER 1970, WICKER, JR. ET AL. See the entire document.	1-29
Y	US, A, 3,720,656, Published 13 MARCH 1973 MANAKA. See the entire document.	1-29

* Special categories of cited documents: ¹⁹

"A" document defining the general state of the art which is not
 considered to be of particular relevance

"E" earlier document but published on or after the international
 filing date

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 which is cited to establish the publication date of another
 citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or
 other means

"P" document published prior to the international filing date but
 later than the priority date claimed

"T" later document published after the international filing date
 or priority date and not in conflict with the application but
 cited to understand the principle or theory underlying the
 invention

"X" document of particular relevance; the claimed invention
 cannot be considered novel or cannot be considered to
 involve an inventive step

"Y" document of particular relevance; the claimed invention
 cannot be considered to involve an inventive step when the
 document is combined with one or more other such docu-
 ments, such combination being obvious to a person skilled
 in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search ² 29 JULY 1986	Date of Mailing of this International Search Report ² 18 AUG 1986
International Searching Authority ¹ ISA/US	Signature of Authorized Officer ¹⁰ N. SAROFIM

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, 16 with indication, where appropriate, of the relevant passages 17	Relevant to Claim No 18
A	US,A, 4,377,490, Published 22 MARCH 1983, SHIRAISHI et al. See the entire document.	1-29
A	US,A, 4,196,271, Published 01 APRIL 1980, YAMADA ET AL. See the entire document.	1-29
A	US,A, 4,102,945, Published 25 JULY 1978, GLEAVE. See the entire document.	1-29
A	US,A, 4,170,585, Published 09 OCTOBER 1979, MOTEGI ET AL. See the entire document.	1-29
A	US,A, 2,765,332, Published 02 OCTOBER 1956, COOVER, JR. ET AL. See the entire document.	1-29
A, P	US,A, 4,556,700, Published 03 DECEMBER 1985, HARRIS ET AL. See the entire document.	1-29
A	US,A, 3,354,128, Published 21 NOVEMBER 1967, WICKER. See the entire document.	1-29
A	US,A, 3,435,012, Published 25 MARCH 1965, NORDLANDER. See the entire document.	1-29